EXHIBIT C

Synthesis and Odor Properties of Substituted Indane-2-carboxaldehydes. Discovery of a New Floral (Muguet) Fragrance Alcohol

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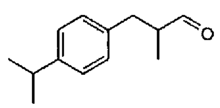
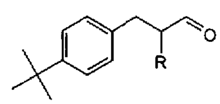
Dedicated to Dr. *Ferdinand Naef* on the occasion of his 65th birthday

Eight substituted indane-2-carboxaldehydes (=2,3-dihydro-1*H*-indene-2-carboxaldehydes), related to conformationally constrained analogues of floral-type odorants, were synthesized in order to examine the effect of modifying the lipophilic part of the odorants (*Schemes 1* and *2*). None of the modified compounds showed better olfactive properties than the original ones (*Tables 1* and *2*), but an intermediate alcohol, **29**, revealed itself as a valuable new member in the family of floral muguet (lily-of-the-valley)-type odorants.

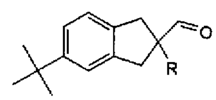
1. Introduction. – Previous studies [1] on conformationally constrained analogues of floral-type perfumery materials such as **1**–**3**, have led to the discovery of new interesting odorants [2], among which compounds **4** and **5** were quite intriguing. Indeed, whereas compound **4** had an odor characterized as 'watery, metallic, aldehydic, green, somewhat fatty, vaguely phenolic', compound **5** was evaluated as typically 'floral, green, 'muguet', *Bourgeonal*®, powerful, tenacious' [1]. This result and related ones pointed to the importance of the steric constraints imposed by the receptor environment in the proximity of the ligand functional group.



(±)-**1** (cyclamen aldehyde)



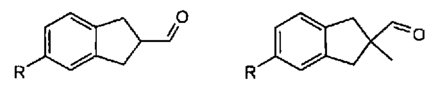
(±)-**2** R = Me (*Lilial*®; *Givaudan*)
3 R = H (*Bourgeonal*®; *Quest Int.*)



(±)-**4** R = Me
(±)-**5** R = H

On the other hand, we suspected that the lipophilic part of the ligands might also play a significant role in their distribution, their affinity, and their orientation in the relevant receptive sites [3]. Accordingly, we undertook to modify the lipophilic part in **4** and **5** and to prepare aldehydes **6** [4]–**13** *via* intermediates derived from 1*H*-indene. We describe in the present paper the synthesis and sensory characterization of this series of aldehydes and their precursor alcohols, which unveiled an olfactorily very interesting new compound.

2. Results and Discussion. – 2.1. *Syntheses.* Aldehyde **6** was prepared by oxidation of alcohol **14** [4a,b,g][5]; as noted earlier [4c,f], **6** is very sensitive to oxidation by air. Aldehydes **7**–**9** were synthesized *via* the common key intermediate **16**; this keto

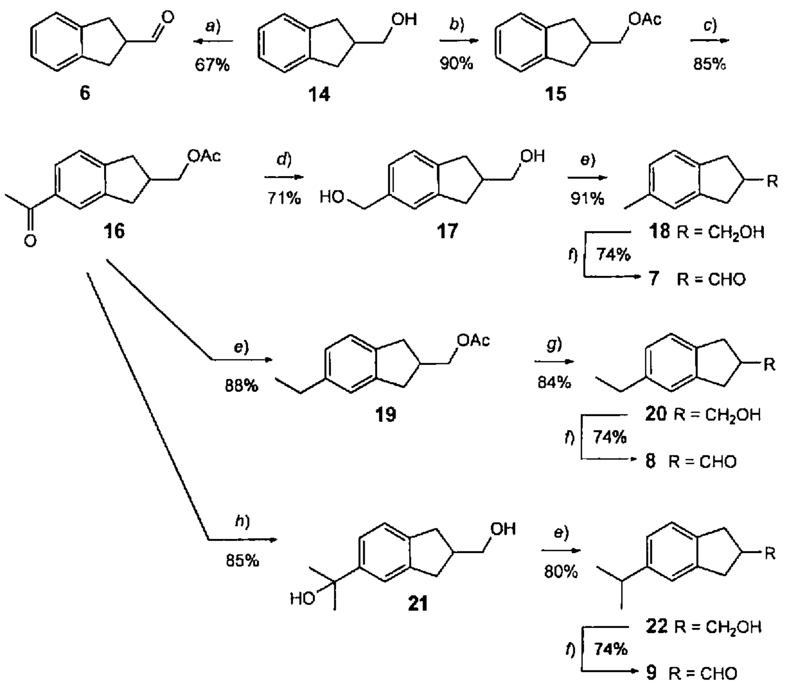


6	R = H	**10**	R = H
7	R = Me	**11**	R = Me
8	R = Et	**12**	R = Et
9	R = Me_2CH	**13**	R = Me_2CH

ester was prepared from alcohol **14** by esterification to acetate **15** [4b] [5a] followed by *Friedel–Crafts* acylation, as shown in *Scheme 1*.

Compound **16** was subjected to the haloform reaction, followed by $LiAlH_4$ reduction to give diol **17**, which was hydrogenolyzed (→ **18**), and then oxidized with pyridinium chlorochromate (PCC) to aldehyde **7**. Next, **16** was hydrogenated to give ester **19**, which was reduced to alcohol **20** and oxidized with PCC to aldehyde **8**. Finally, *Grignard* reaction of **16** produced diol **21**, which, as above, was hydrogenolyzed (→ **22**) and oxidized to afford aldehyde **9**.

Scheme 1. *Synthesis of Aldehydes* **6**–**9**

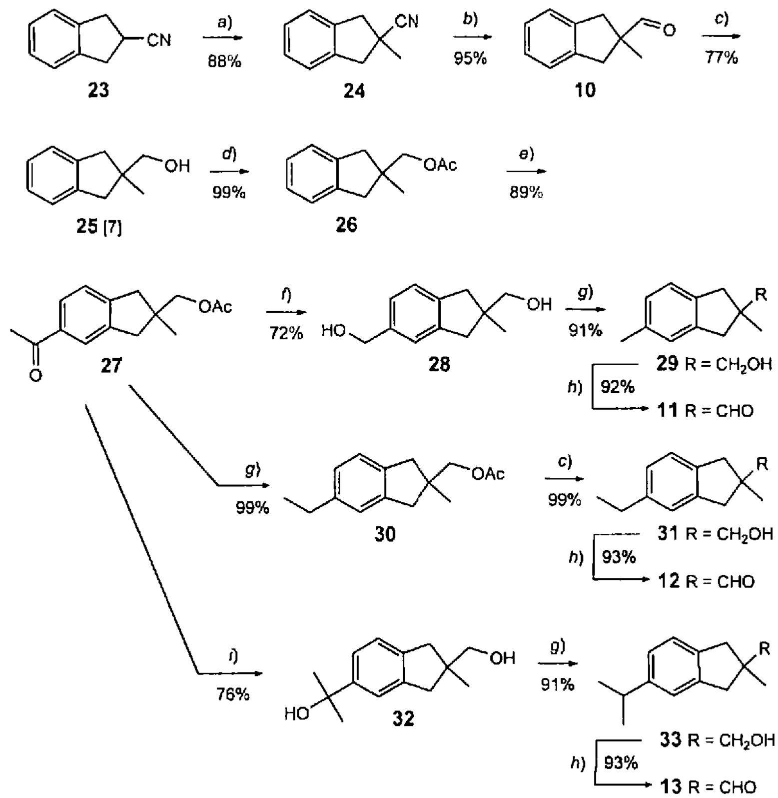


a) Pyridinium chlorochromate (PCC), CH_2Cl_2, r.t. *b*) Ac_2O, pyridine, r.t., 3.5 h. *c*) AcCl, $AlCl_3$, CH_2Cl_2, 0° → r.t., 1 h. *d*) 1. NaOCl, H_2O, dioxane, 60°, 17 h; 2. $LiAlH_4$, THF, reflux, 16 h. *e*) H_2 (1 atm), 10% Pd/C, AcOEt, r.t., 16 h. *f*) PCC, CH_2Cl_2, r.t., 4 h. *g*) $LiAlH_4$, Et_2O, r.t., 1.5 h. *h*) MeMgCl, THF, r.t. → 60°, 2 h.

Turning then to the series of 2-methylindane-2-carboxaldehydes **10**–**13**, the attempted alkylation of **6** gave **10** in only low yield and purity; aldehyde **10** was preferentially prepared in good yield by alkylation of nitrile **23** [6] (→ **24**), followed by reduction (*Scheme 2*). For the synthesis of aldehydes **11**–**13**, we applied the same principle as above, which allowed to use the keto ester **27** as a common intermediate. Thus, **10** was reduced to alcohol **25** [7], which was esterified (→ **26**) and acylated to afford **27**; from **27**, aldehydes **11**–**13** were synthesized *via* **28**–**33** in the same manner as above.

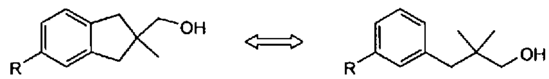
2.2. *Olfactory Evaluation.* The results of the olfactory evaluation of aldehydes **6**–**13** are given in *Table 1*, and those of the alcohol precursors are shown in *Table 2*. The unexpected result of this work was the powerful floral muguet(lily-of-the-valley)-type odor

Scheme 2. *Synthesis of Aldehydes* **10**–**13**



a) Lithium diisopropylamide (LDA), MeI, THF, –78° → r.t. → 50°, 1.5 h. *b*) Diisobutylaluminium hydride (DIBAL-H), toluene, r.t., 1.5 h. *c*) $LiAlH_4$, Et_2O, r.t., 15 h; *d*) Ac_2O, pyridine, r.t., 36 h. *e*) AcCl, $AlCl_3$, CH_2Cl_2, 0°, 1.5 h. *f*) 1. NaOCl, H_2O, dioxane, 60°, 16 h; 2. $LiAlH_4$, THF, reflux, 16 h. *g*) H_2 (1 atm), 10% Pd/C, AcOEt, r.t., 18 h. *h*) PCC, CH_2Cl_2, r.t., 3 h. *i*) MeMgCl, THF, r.t. → 60°, 1.5 h.

of the intermediate alcohol **29** [8] (see *Table 2*), noticed as soon as we isolated it[1]). Quickly, however, the structural parenthood of alcohol **29** with the floral odorant *Majantol*® (**34**) [9] was recognized. In fact, alcohol **29** can be considered as a conformationally restricted analogue of **34**, and the same relationship holds for alcohol **25** and the floral odorant **35**, known as 'muguet alcohol' [9b][10].



29 R = Me
25 R = H

34 R = Me (*Majantol*®; *Wacker*)
35 R = H (Muguet alcohol; *Symrise*)

Table 1. *Odor Description of Aldehydes* **6**–**13**. Excepting **6** and **10**, all compounds are racemates.

	Odor description
6	'Aldehydic, green, grassy, ozonic, slightly metallic, cuminic, very powerful, aggressive'
7	'Aldehydic, floral-muguet, soapy, fatty, slightly lemon'
8	'Aldehydic, metallic, muguet, citrus'
9	'Aldehydic, green, citrus, ozone, cyclamen aldehyde, metallic, *Bourgeonal*®, but weaker'
10	'Phenolic, aldehydic, green'
11	'Aldehydic, green, *Bourgeonal*®, slightly fatty, fertilizer'
12	'Aldehydic, metallic, fatty, perillic'
13	'Aldehydic, metallic, ozone, green, citrus'

Table 2. *Odor Description of Precursor Alcohols* **14**, **18**, **20**, **22**, **25**, **29**, **31**, *and* **33**. Excepting **14** and **25**, all compounds are racemates.

	Odor description
14	'Leather, old shoes, ammunition, fatty'
18	'Floral, phenolic, fatty'
20	'Odorless'
22	'Odorless'
25	'Floral, *Lilial*®, muguet, hydroxycitronellal'
29	'*Lilial*®, hydroxycitronellal, *Mayol*®, muguet'
31	'Vaguely floral, weak'
33	'Floral, linalool, very weak'

In conclusion, none of the initially targeted aldehydes had better olfactive properties than the already established odorants of this class, but the intermediate alcohol **29** revealed itself as a valuable new member in the family of floral muguet(lily-of-the-valley)-type odorants [11].

We gratefully acknowledge the collaboration of Mr. *W. Thommen* and Mr. *R. Brauchli* for the NMR analysis. We wish to thank Dr. *P.-A. Blanc* for the evaluation of olfactory properties, and Dr. *R. L. Snowden* and Dr. *C. Fehr* for stimulating discussions.

[1]) See accompanying publication for an alternative synthesis of **29** and the characterization of the enantiomers of **29**.

Experimental Part

General. All reactions were performed under N_2. GLC: *Hewlett-Packard 5890* or *6890* instrument equipped with a flame-ionization detector coupled to a *Hewlett-Packard 3395* or *3396A* integrator; capillary columns *Chrompack CP-Wax-52 CB* (10 m, 0.25 mm i.d.) and *CP-Sil-5 CB* (10 m, 0.25 mm i.d.). TLC: silica gel *60 F 254* (layer thickness 0.25 mm; *Merck*). Column chromatography (CC): silica gel *60* (0.063–0.2 mm, 70–270 mesh, ASTM; *Merck*). Bulb-to-bulb distillation: *Büchi GKR-50* or *GRK-51* oven; b.p. correspond to the air temp. IR Spectra (liquid film or solid): *Perkin-Elmer 297* or *1600-FTIR* spectrometers; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra ($CDCl_3$): *Bruker AMX-360*, *DPX-400*, or *AV-500* spectrometers; δ in ppm downfield from $SiMe_4$, *J* in Hz. MS: *HP 5972* or *5973 MSD* (70 eV); in *m/z* (intensity in % rel. to the base peak (100%)).

1. *General Procedure A* (*G.P.A*) *for the Hydrogenolysis of Benzylic Alcohols.* To a soln. of the benzylic alcohol in AcOEt was added 10% Pd/C (*ca.* 0.02 equiv.), and the mixture was shaken under H_2 (1 atm) at r.t. until no more starting material was detected by GC (16–46 h). The catalyst was filtered off and the filtrate evaporated.

2. *General Procedure B* (*G.P.B*) *for the Oxidation of Alcohols to Aldehydes with Pyridinium Chlorochromate* (PCC). To a stirred suspension of PCC (1.5 equiv.) in CH_2Cl_2 at r.t. was added dropwise a soln. of the alcohol (1.0 equiv.) in CH_2Cl_2, and the mixture was stirred at r.t. during 3–5 h. The mixture was diluted with an excess of Et_2O, filtered through a short column of *Florisil®* (*Acros Organics*), and evaporated.

3. *Compounds* **6**–**9**. *Indane-2-carboxaldehyde* (=*2,3-Dihydro-1*H*-indene-2-carboxaldehyde*; **6**). According to the *G.P.B*, indane-2-methanol (**14**; 3.20 g, purity 97%, 20.9 mmol) was converted to crude **6**, to which was added 0.5% (*w/w*) BHT (=2,6-di(*tert*-butyl)-4-methylphenol). Bulb-to-bulb distillation (oven temp. 50–60°/0.2 mbar) afforded **6** (2.10 g, 67%; purity 98%). Colorless oil. IR: 3050, 2910, 2840, 2710, 1720, 1480, 1450, 740. ^1H-NMR: 9.72 (*d*, *J*=2, 1 H); 7.20 (*m*, 2 H); 7.13 (*m*, 2 H); 3.24 (*m*, 3 H); 3.15 (*m*, 2 H). ^{13}C-NMR: 202.8 (*d*); 141.1 (2*s*); 126.8 (2*d*); 124.6 (2*d*); 50.6 (*d*); 32.9 (2*t*). MS: 146 (67, M^+), 131 (16), 128 (18), 115 (100), 91 (26), 89 (14), 63 (15), 51 (9), 39 (12), 29 (8).

Indan-2-ylmethyl Acetate (=*2,3-Dihydro-1*H*-indene-2-methanol Acetate*; **15**). To a stirred soln. of indane-2-methanol (**14**; 3.29 g, 22 mmol) in pyridine (25 ml) at r.t. was added Ac_2O (25 ml), and the mixture was stirred at r.t. during 3.5 h. The mixture was evaporated and the residue co-evaporated 3× from toluene. Bulb-to-bulb distillation (oven temp. 90–100°/0.8 mbar) gave **15** (3.98 g, 90%; purity 95%). Colorless oil. IR: 3015, 2940, 2835, 1730, 1360, 1235, 1040, 745. ^1H-NMR: 7.16 (*m*, 4 H); 4.10 (*d*, *J*=7, 2 H); 3.07 (*dd*, *J*=15, 8, 2 H); 2.80 (*m*, 1 H); 2.73 (*dd*, *J*=15, 7, 2 H); 2.06 (*s*, 3 H). ^{13}C-NMR: 171.2 (*s*); 142.3 (2*s*); 126.4 (2*d*); 124.6 (2*d*); 67.6 (*t*); 38.2 (*d*); 39.9 (*t*); 20.9 (*q*). MS: 190 (1, M^+), 130 (100), 129 (67), 115 (64), 91 (12), 77 (4), 63 (5), 51 (4), 43 (34), 39 (6).

(±)-(5-Acetyl-indan-2-yl)methyl Acetate (=*(±)-1-[2-[(Acetyloxy)methyl]-2,3-dihydro-1*H*-indene-5-yl]-ethanone*; **16**). To a stirred suspension of $AlCl_3$ (18.7 g, 140 mmol) in CH_2Cl_2 (80 ml) at 20° was added dropwise AcCl (9.9 ml, 140 mmol), and the mixture was stirred at 20° during 1.5 h. The mixture was cooled to 0°, and a soln. of **15** (5.28 g, 27 mmol) in CH_2Cl_2 (15 ml) was added dropwise. The mixture was stirred at 0–4° during 1 h and poured on CH_2Cl_2/ice/brine. The org. phase was washed with brine (2×), sat. aq. $NaHCO_3$ soln., and brine, dried (Na_2SO_4), and evaporated to a yellow oil (6.3 g). Bulb-to-bulb distillation (oven temp. 150°/0.4 mbar) gave **16** (5.83 g, 85%; purity 93%). Yellow oil. IR: 2940, 2830, 1730, 1670, 1600, 1420, 1360, 1235, 1035, 820. ^1H-NMR: 7.80 (*d*, *J*=1, 1 H); 7.77 (*dd*, *J*=8, 1, 1 H); 7.27 (*d*, *J*=8, 1 H); 4.10 (*d*, *J*=7, 1 H); 3.12 (*dd*, *J*=15, 8, 2 H); 2.86 (*m*, 1 H); 2.78 (*dd*, *J*=15, 7, 2 H); 2.57 (*s*, 3 H); 2.06 (*s*, 3 H). ^{13}C-NMR: 198.0 (*s*); 171.1 (*s*); 148.3 (*s*); 143.0 (*s*); 136.1 (*s*); 127.2 (*d*); 124.6 (*d*); 124.5 (*d*); 67.2 (*t*); 38.3 (*d*); 36.0 (*t*); 35.6 (*t*); 26.7 (*q*); 20.9 (*q*). MS: 232 (1, M^+), 217 (3), 172 (37), 157 (100), 129 (28), 115 (18), 89 (3), 77 (3), 63 (4), 51 (3), 43 (63).

(±)-Indane-2,5-dimethanol (=*(±)-2,3-Dihydro-1*H*-indene-2,5-dimethanol*; **17**). Bleach (13–14% NaOCl in H_2O; 21.5 ml, 37.5 mmol) was heated to 55°, and a soln. of **16** (2.91 g, purity 95%, 12.5 mmol) in dioxane (22 ml) was added dropwise during 5 min (slightly exothermic: temp. → 70°), and the mixture was heated to 70° during 17 h. The cooled mixture was poured on Et_2O/sat. aq. $NaHSO_3$ soln. and H_2O. The aq. phase was acidified with 10% aq. HCl soln. and extracted with Et_2O. This org. phase was washed with brine (3×), dried (Na_2SO_4), and evaporated to a viscous yellow oil (3.459 g), containing the acid. A soln. of this crude product in THF (50 ml) was added to a stirred suspension of $LiAlH_4$ (1.75 g, 46 mmol) in THF (30 ml) at r.t. (exothermic: temp. → 53°). After 15 h at r.t., the mixture was poured on Et_2O/10% aq. NaOH soln. The org. phase was washed with sat. aq. $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated to a solid (2.23 g, 71%; purity 71%). Three crystallizations from AcOEt at 0° afforded pure **17**. Colorless crystals. M.p. 115.5°. IR (solid): 3352, 3275, 2942, 2905, 2847, 1437, 1359, 1071, 1043, 1021, 821. ^1H-NMR (CD_3OD): 7.16 (br. *s*, 1 H); 7.12 (*d*, *J*=8, 1 H); 7.07 (*d*, *J*=8, 1 H); 4.87 (*s*, 2 OH); 4.53 (*s*, 2 H); 3.51 (*d*, *J*=7, 2 H); 2.98 (*m*, 2 H); 2.70 (*m*, 1 H); 2.62 (*m*, 2 H). ^{13}C-NMR

(CD_3OD): 144.2 (*s*); 143.1 (*s*); 140.7 (*s*); 126.4 (*d*); 125.3 (*d*); 124.4 (*d*); 66.6 (*t*); 65.4 (*t*); 43.0 (*d*); 36.6 (*t*); 36.4 (*t*). MS: 178 (52, M^+), 160 (13), 145 (12), 142 (17), 129 (100), 115 (60), 91 (38), 77 (13), 65 (9), 63 (9), 51 (9), 39 (11), 31 (29).

(±)-5-Methylindane-2-methanol (= *(±)-2,3-Dihydro-5-methyl-1*H*-indene-2-methanol*; **18**). According to the *G.P.A*, with **17** (0.9 g, 5 mmol). Bulb-to-bulb distillation (oven temp. → 170°/0.3 mbar) followed by crystallization from pentane at 0° gave **18** (0.64 g, 79%). Colorless crystals. M.p. 41–41.5°. IR: 3580, 2980, 2910, 1485, 1430, 1025, 995, 810. ^{1}H-NMR: 7.08 (*d*, *J* = 8, 1 H); 7.01 (br. *s*, 1 H); 6.94 (br. *d*, 1 H); 3.62 (*d*, *J* = 7, 2 H); 3.01 (*dd*, *J* = 17, 10, 2 H); 2.68 (*m*, 3 H); 2.30 (*s*, 3 H); 1.86 (br. *s*, OH). ^{13}C-NMR: 142.8 (*s*); 139.6 (*s*); 135.8 (*s*); 127.0 (*d*); 125.3 (*d*); 124.3 (*d*); 66.5 (*t*); 41.6 (*d*); 35.7 (*t*); 21.2 (*q*). MS: 162 (34, M^+), 144 (26), 129 (100), 115 (29), 91 (16), 77 (8), 65 (4), 63 (6), 51 (7), 39 (7), 31 (15).

(±)-5-Methylindane-2-carboxaldehyde (= *(±)-2,3-Dihydro-5-methyl-1*H*-indene-2-carboxaldehyde*; **7**). According to the *G.P.B*, with **18** (0.30 g, 1.9 mmol). Bulb-to-bulb distillation (oven temp. 75°/0.15 mbar) afforded **7** (0.24 g, 77%; purity 97%). Colorless liquid. IR: 3000, 2840, 2700, 1715, 1485, 1430, 805. ^{1}H-NMR: 9.75 (*d*, *J* = 2, 1 H); 7.11 (*d*, *J* = 8, 1 H); 7.05 (br. *s*, 1 H); 6.97 (br. *d*, *J* = 8, 1 H); 3.24 (*m*, 3 H); 3.13 (*m*, 2 H); 2.31 (*s*, 3 H). ^{13}C-NMR: 203.0 (*d*); 141.3 (*s*); 138.0 (*s*); 136.5 (*s*); 127.6 (*d*); 125.3 (*d*); 124.3 (*d*); 50.9 (*d*); 32.8 (*t*); 32.6 (*t*); 21.2 (*q*). MS: 160 (100, M^+), 145 (72), 130 (34), 115 (98), 91 (39), 77 (23), 65 (13), 63 (19), 51 (25), 39 (24), 29 (40).

(±)-(5-Ethylindan-2-yl)methyl Acetate (= *(±)-5-Ethyl-2,3-dihydro-1*H*-indene-2-methanol Acetate*; **19**). According to the *G.P.A*, with **16**. Bulb-to-bulb distillation (oven temp. 180°/0.1 mbar) gave **19** (1.70 g, 88%; purity 94%). Colorless oil. IR: 3000, 2960, 2930, 2840, 1730, 1485, 1435, 1360, 1235, 1035, 820. ^{1}H-NMR: 7.10 (*d*, *J* = 8, 1 H); 7.04 (br. *s*, 1 H); 6.97 (br. *d*, *J* = 8, 1 H); 4.10 (*d*, *J* = 7, 2 H); 3.03 (*m*, 2 H); 2.80 (*m*, 1 H); 2.70 (*m*, 2 H); 2.60 (*q*, *J* = 8, 2 H); 2.06 (*s*, 3 H); 1.22 (*t*, *J* = 8, 3 H). ^{13}C-NMR: 171.2 (*s*); 142.6 (*s*); 142.5 (*s*); 139.5 (*s*); 126.1 (*d*); 124.4 (*d*); 124.1 (*d*); 67.7 (*t*); 38.4 (*d*); 35.9 (*t*); 35.6 (*t*); 28.7 (*t*); 20.9 (*q*); 16.0 (*q*). MS: 218 (6, M^+), 158 (45), 143 (56), 129 (100), 115 (31), 91 (8), 77 (5), 65 (3), 63 (3), 51 (3), 43 (32), 39 (4).

(±)-5-Ethylindane-2-methanol (= *(±)-5-Ethyl-2,3-dihydro-1*H*-indene-2-methanol*; **20**). To a stirred suspension of $LiAlH_4$ (0.43 g, 11.3 mmol) in Et_2O (10 ml) at r.t. was added dropwise a soln. of **19** (1.65 g, purity 94%, 7.5 mmol) in Et_2O (15 ml), and the mixture was stirred at r.t. during 1.5 h. The mixture was cooled to 0°, 10% aq. NaOH soln. (2.5 ml) was added carefully, and the mixture was stirred during 1 h (→ r.t.). Na_2SO_4 was added and the mixture filtered and evaporated (1.26 g). Bulb-to-bulb distillation (oven temp. → 205°/0.1 mbar) gave **20** (1.19 g, 84%; purity > 99%). Colorless oil. IR: 3320 (br.), 3000, 2960, 2920, 2860, 1485, 1430, 1035, 815. ^{1}H-NMR: 7.10 (*d*, *J* = 8, 1 H); 7.04 (br. *s*, 1 H); 6.97 (br. *d*, *J* = 8, 1 H); 3.63 (*d*, *J* = 7, 2 H); 3.02 (*m*, 2 H); 2.69 (*m*, 3 H); 2.60 (*q*, *J* = 8, 2 H); 1.94 (br. *s*, OH); 1.21 (*t*, *J* = 8, 3 H). ^{13}C-NMR: 142.9 (*s*); 142.5 (*s*); 139.9 (*s*); 125.9 (*d*); 124.4 (*d*); 124.1 (*d*); 66.6 (*t*); 6 (5 (*t*); 41.6 (*d*); 35.7 (*t*); 35.4 (*t*); 28.7 (*t*); 16.0 (*q*). MS: 176 (39, M^+), 158 (15), 143 (67), 129 (100), 115 (34), 91 (12), 77 (7), 65 (4), 63 (5), 51 (5), 39 (5), 31 (10).

(±)-5-Ethylindane-2-carboxaldehyde (= *(±)-5-Ethyl-2,3-dihydro-1*H*-indene-2-carboxaldehyde*; **8**). According to *G.P.B*, with **20** (1.12 g, 6.4 mmol). Bulb-to-bulb distillation (oven temp. → 95°/0.2 mbar) gave **8** (0.85 g, 74%; purity 97%). Colorless oil. IR: 3000, 2960, 2840, 2700, 1715, 1485, 1435, 820. ^{1}H-NMR: 9.74 (*d*, *J* = 2, 1 H); 7.13 (*d*, *J* = 8, 1 H); 7.07 (br. *s*, 1 H); 6.99 (br. *d*, *J* = 8, 1 H); 3.24 (*m*, 3 H); 3.13 (*m*, 2 H); 2.60 (*q*, *J* = 8, 2 H); 1.21 (*t*, *J* = 8, 3 H). ^{13}C-NMR: 203.0 (*d*); 143.1 (*s*); 141.3 (*s*); 138.3 (*s*); 126.5 (*d*); 124.4 (*d*); 124.1 (*d*); 50.9 (*d*); 32.9 (*t*); 32.6 (*t*); 28.7 (*t*); 15.9 (*q*). MS: 174 (71, M^+), 159 (19), 156 (5), 145 (100), 141 (19), 129 (80), 117 (45), 115 (58), 91 (18), 77 (11), 65 (8), 63 (10), 51 (9), 39 (9), 29 (13).

(±)-2-[2-(Hydroxymethyl)indan-5-yl]propan-2-ol (= *(±)-2,3-Dihydro-α^5,α^5-dimethyl-1*H*-indene-2,5-dimethanol*; **21**). A stirred 22% MeMgCl soln. in THF (16.7 g, 46 mmol; *Fluka*) at r.t. was diluted with THF (50 ml), and a soln. of **16** (2.92 g, purity 92%, 11.6 mmol) in THF (20 ml) was added dropwise during 5 min (exothermic: temp. → 44°). The mixture was heated to 60° during 2 h, then cooled, and poured into Et_2O/sat. aq. NH_4Cl soln./ice. The org. phase was washed with sat. aq. $NaHCO_3$ soln. and brine (2×), dried (Na_2SO_4), and evaporated (3.14 g). Bulb-to-bulb distillation (oven temp. → 200/0.1 mbar) afforded a major fraction (1.76 g, 85%) containing 85% of **21** and 15% of monodehydrated product. IR: 3570, 3400, 2960, 2920, 1430, 1360, 1315, 1160, 1105, 1025, 950, 830. ^{1}H-NMR: 7.32 (br. *s*, 1 H); 7.24 (br. *d*, *J* = 8, 1 H); 7.13 (*d*, *J* = 8, 1 H); 3.61 (*d*, *J* = 7, 2 H); 3.02 (*m*, 2 H); 2.69 (*m*, 3 H); 2.22 (br. *s*, OH); 1.55 (*s*, 6 H). ^{13}C-NMR: 147.5 (*s*); 142.8 (*s*); 141.1 (*s*); 124.2 (*d*); 122.5 (*d*); 120.7 (*d*); 72.4 (*s*); 66.3 (*t*); 41.6 (*d*); 35.8 (*t*); 35.3 (*t*); 31.8 (2*q*). MS: 206 (16, M^+), 191 (85), 173 (9), 131 (27), 115 (22), 91 (10), 77 (5), 59 (8), 43 (100), 31 (10).

(±)-5-Isopropylindane-2-methanol (= *(±)-2,3-Dihydro-5-isopropyl-1*H*-indene-2-methanol*; **22**). According to the *G.P.A*, with **21** (containing monodehydrated product; 1.90 g, 9.2 mmol). Bulb-to-bulb distillation (oven temp. → 140°/0.3 mbar) afforded **22** (1.44 g, 80%; purity 99%). Colorless oil. IR: 3320 (br.), 2960, 2920, 2860, 1485, 1455, 1430, 1030, 815. ^{1}H-NMR: 7.11 (*d*, *J* = 8, 1 H); 7.07 (br. *s*, 1 H); 7.00 (br. *d*, *J* = 8, 1 H); 3.64 (*d*,

$J=7$, 2 H); 3.03 (*m*, 2 H); 2.87 (*sept.*, $J=7$, 1 H); 2.69 (*m*, 3 H); 1.86 (br. *s*, OH); 1.23 (*d*, $J=7$, 6 H). ^{13}C-NMR: 147.2 (*s*); 142.8 (*s*); 140.1 (*s*); 124.4 (*d*); 122.6 (*d*); 66.5 (*d*); 41.6 (*d*); 35.8 (*t*); 34.0 (*d*); 24.2 (2*q*). MS: 190 (42, M^+), 175 (45), 157 (100), 142 (25), 129 (71), 115 (40), 91 (15), 77 (7), 65 (5), 63 (5), 51 (5), 43 (10), 31 (23).

(±)-5-Isopropylindane-2-carboxaldehyde (= *(±)-2,3-Dihydro-5-isopropyl-1*H*-indene-2-carboxaldehyde*; **9**). According to the *G.P. B*, with **22** (1.44 g, purity 99%, 7.5 mmol). Bulb-to-bulb distillation (oven temp. → 130°/0.2 mbar) gave **9** (1.09 g, 74%; purity 96%). Colorless oil. IR: 2950, 2920, 2870, 2700, 1715, 1480, 1430, 1375, 1050, 820. ^{1}H-NMR: 9.74 (*d*, $J=2$, 1 H); 7.14 (*d*, $J=8$, 1 H); 7.09 (br. *s*, 1 H); 7.03 (br. *d*, $J=8$, 1 H); 3.25 (*m*, 3 H); 3.14 (*m*, 2 H); 1.87 (*sept.*, $J=7$, 1 H); 1.23 (*d*, $J=7$, 6 H). ^{13}C-NMR: 203.0 (*d*); 147.8 (*s*); 141.3 (*s*); 138.5 (*s*); 125.1 (*d*); 124.4 (*d*); 122.5 (*d*); 50.9 (*d*); 34.0 (*d*); 32.9 (*t*); 32.6 (*t*); 24.2 (2*q*). MS: 188 (92, M^+), 173 (88), 155 (43), 145 (100), 143 (70), 128 (80), 115 (78), 91 (28), 77 (14), 65 (12), 63 (13), 39 (18), 29 (21).

4. *Compounds* **10**–**13**. *2-Methylindane-2-carbonitrile* (= *2,3-Dihydro-2-methyl-1*H*-indene-2-carbonitrile*; **24**). To 1.6M BuLi in hexane (58 ml, 93 mmol; *Fluka pract.*) in THF (40 ml) at −78° was added dropwise within 5 min ^{i}Pr$_2$NH (12.5 ml, 88 mmol) and the mixture was stirred at −78° during 30 min. A soln. of indane-2-carbonitrile (=2,3-dihydro-1*H*-indene-2-carbonitrile; **23**; 6.32 g, 44 mmol) in THF (50 ml) was added dropwise within 5 min, and the mixture was stirred at −78° during 1.5 h. The mixture was allowed to warm up to −40°, and MeI (4.2 ml, 66 mmol; *Fluka purum*) was added dropwise. The mixture was stirred during 1 h (−40° → −10°) and then poured on Et_2O/H_2O/ice. The org. phase was washed with 10% aq. HCl soln., H_2O, sat. aq. $NaHCO_3$ soln., and brine, dried (Na_2SO_4), and evaporated to a yellow liquid (7.25 g). Two bulb-to-bulb distillations (oven temp. 40–65°/0.3 mbar) afforded a product which solidified on standing: **24** (6.14 g, 83%; purity 94%). Crystallization from pentane at 0° gave an anal. sample. Colorless crystals. M.p. 60–60.5°. IR: 2960, 2930, 2840, 2230, 1480, 1450, 1430, 1375. ^{1}H-NMR: 7.20 (*s*, 4 H); 3.47 (*d*, $J=16$, 2 H); 3.00 (*d*, $J=16$, 2 H); 1.50 (*s*, 3 H). ^{13}C-NMR: 139.3 (2*s*); 127.3 (2*d*); 125.4 (*s*); 124.7 (2*d*); 45.5 (2*t*); 36.9 (*s*); 25.2 (*q*). MS: 157 (100, M^+), 142 (75), 130 (73), 115 (79), 105 (10), 103 (10), 89 (18), 77 (16), 63 (22), 51 (19), 39 (18).

2-Methylindane-2-carboxaldehyde (= *2,3-Dihydro-2-methyl-1*H*-indene-2-carboxaldehyde*; **10**). To a stirred soln. of **24** (17.7 g, 110 mmol) in toluene (100 ml) at r.t. was added dropwise during 25 min 1.5M DIBAL-H in toluene (120 ml, 180 mmol; *Aldrich*), while maintaining the temp. at 25° with a water bath. After 1 h at r.t., the mixture was poured slowly into Et_2O/10% aq. HCl soln./ice. The org. phase was washed with brine, sat. aq. $NaHCO_3$ soln., and brine, dried (Na_2SO_4), and evaporated to a yellow liquid (16.8 g, 95%; purity 99%). Bulb-to-bulb distillation (oven temp. 55–100°/1.0 mbar) gave **10**. Colorless liquid. IR: 2960, 2920, 2830, 2700, 1720, 1475, 1450, 1425, 745. ^{1}H-NMR: 7.16 (*m*, 4 H); 3.34 (*d*, $J=16$, 2 H); 2.74 (*d*, $J=16$, 2 H); 1.28 (*s*, 3 H). ^{13}C-NMR: 203.9 (*d*); 140.9 (2*s*); 126.8 (2*d*); 124.7 (2*d*); 54.2 (*s*); 40.8 (2*t*); 20.9 (*q*). MS: 160 (42, M^+), 145 (100), 131 (33), 115 (48), 91 (44), 77 (11), 65 (8), 63 (10), 51 (9), 39 (8).

2-Methylindane-2-methanol (= *2,3-Dihydro-2-methyl-1*H*-indene-2-methanol*; **25**). To a stirred suspension of $LiAlH_4$ (3.80 g, 100 mmol) in Et_2O (50 ml) at r.t. was added during 15 min a soln. of **10** (16.8 g, purity 92%, 100 mmol) in Et_2O (100 ml). After 1 h at r.t, the mixture was cooled to 4°, and 10% aq. NaOH soln. (19 ml) was added carefully. The mixture was stirred at r.t. during 1.5 h, Na_2SO_4 was added, and the mixture was filtered and evaporated to a colorless liquid which solidified on standing (13.7 g). Crystallization from pentane at 0° gave **25** (13.4 g, 77%; purity 94%). Colorless crystals. M.p. 47–47.5°. IR: 3350 (br.), 2920, 1450, 1035, 740. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.14 (*m*, 4 H); 3.48 (*s*, 2 H); 2.90 (*d*, $J=16$, 2 H); 2.63 (*d*, $J=16$, 2 H); 2.04 (br., OH); 1.16 (*s*, 3 H). ^{13}C-NMR (90.5 MHz, $CDCl_3$): 142.5 (2*s*); 126.2 (2*d*); 124.8 (2*d*); 70.3 (*t*); 44.9 (*s*); 42.7 (2*t*); 24.0 (*q*). MS: 162 (25, M^+), 144 (12), 129 (100), 115 (25), 104 (10), 91 (21), 77 (8), 63 (6), 51 (6), 39 (6), 31 (7).

(2-Methylindan-2-yl)methyl Acetate (= *2,3-Dihydro-2-methyl-1*H*-indene-2-methanol Acetate*; **26**). To a stirred soln. of **25** (13.7 g, purity 96%, 79.6 mmol) in pyridine (50 ml) at r.t. was added Ac_2O (50 ml), and the mixture was stirred at r.t. during 1.5 h. The mixture was evaporated, co-evaporated 3× from toluene (17.5 g), and bulb-to-bulb distilled (oven temp. 70→95°/0.3 mbar): **26** (16.2, 49%; purity > 99%). Colorless oil. IR: 2950, 2920, 2830, 1730, 1450, 1365, 1235, 1040, 740. ^{1}H-NMR: 7.14 (*m*, 4 H); 2.93 (*d*, $J=16$, 2 H); 2.18 (*d*, $J=16$, 2 H); 2.04 (*s*, 2 H); 1.17 (*s*, 3 H). ^{13}C-NMR: 171.3 (*s*); 142.1 (2*s*); 126.3 (2*d*); 124.8 (2*d*); 71.3 (*t*); 43.2 (*s*); 43.1 (2*t*); 24.3 (*q*); 20.9 (*q*). MS: 204 (1, M^+), 144 (36), 129 (100), 115 (16), 91 (10), 77 (4), 63 (3), 51 (3), 43 (21), 39 (3).

(±)-(5-Acetyl-2-methylindan-2-yl)methyl Acetate (= *(±)-1-{2-[(Acetyloxy)methyl]-2,3-dihydro-2-methyl-1*H*-inden-5-yl}ethanone*; **27**). To a stirred suspension of $AlCl_3$ (53.3 g, 400 mmol) in CH_2Cl_2 (200 ml) at 0–4° was added within 13 min AcCl (28.4 ml, 400 mmol), and the mixture was stirred at 4° until the $AlCl_3$ was dissolved (5 min). A soln. of **26** (16.2 g, 79.6 mol) in CH_2Cl_2 (100 ml) was added dropwise during 15 min, while maintaining the temp. at *ca.* 4°, and the mixture was stirred at *ca.* 4° during 1 h. The mixture was added to CH_2Cl_2/brine/ice, the org. phase washed with brine (2×), sat. aq. $NaHCO_3$ soln., and brine, dried (Na_2SO_4),

and evaporated to a green oil (18.2 g). Bulb-to-bulb distillation (oven temp. 145 → 200°/0.4 mbar) gave **27** (17.5, 89%; purity 96%). Yellow liquid. IR: 2950, 2920, 2830, 1730, 1670, 1600, 1565, 1420, 1355, 1275, 1235, 1040, 825. ^{1}H-NMR: 7.78 (*s*, 1 H); 7.76 (*d*, *J* = 8, 1 H); 7.25 (*d*, *J* = 8, 1 H); 2.98 (*d*, *J* = 16, 2 H); 2.73 (*d*, *J* = 16, 2 H); 2.58 (*s*, 3 H); 2.06 (*s*, 3 H); 1.18 (*s*, 3 H). ^{13}C-NMR: 198.0 (*s*); 171.2 (*s*); 148.2 (*s*); 142.8 (*s*); 136.1 (*s*); 127.2 (*d*); 124.8 (*d*); 124.7 (*d*); 70.9 (*t*); 43.6 (*s*); 43.1 (*t*); 42.7 (*t*); 26.7 (*q*); 24.2 (*q*); 20.8 (*q*). MS: 248 (6, M^+), 186 (33), 171 (76), 157 (7), 143 (22), 128 (26), 115 (13), 91 (3), 77 (5), 63 (3), 51 (3), 43 (100), 39 (2).

(±)-2-Methylindane-2,5-dimethanol (= *(±)-2,3-Dihydro-2-methyl-1*H*-indene-2,5-dimethanol*; **28**). To stirred bleach (13–14% aq. NaOCl soln.; 34 ml, 59 mmol) at 55° was added a soln. of **27** (4.88 g, purity 95%, 19.8 mmol) in dioxane (40 ml): the reaction was exothermic (temp. → 75°) and the mixture became a cloudy emulsion. After 16 h at *ca.* 64°, the cooled mixture was poured on Et_2O/sat. aq. $NaHSO_3$ soln./ice water. The aq. phase was further acidified with 10% aq. HCl soln. in the presence of Et_2O, and the combined org. phase was washed with brine (3×), dried (Na_2SO_4), and evaporated crude intermediate hydroxy acid (5.72 g), which was used as such for the next step.

To a stirred suspension of $LiAlH_4$ (2.62 g, 69 mmol) in THF (67 ml) at r.t. was added dropwise within 15 min a soln. of the crude hydroxy acid (5.72 g) in THF (50 ml), and the mixture was heated to reflux (64°) during 16 h. The mixture was cooled to 4°, 10% aq. NaOH soln. (13.1 ml) added cautiously, the mixture stirred during 1 h (→ r.t.), Na_2SO_4 added, and the mixture filtered and evaporated. Flash column chromatography (SiO_2 (200 g), Et_2O/cyclohexane 9:1) gave **28** (2.83 g, 72%; purity 96%). Colorless syrup. IR: 3300 (br.), 2950, 2850, 1485, 1430, 1365, 1030, 820. ^{1}H-NMR: 7.14 (*s*, 1 H); 7.12 (*d*, *J* = 8, 1 H); 7.08 (*d*, *J* = 8, 1 H); 4.58 (*s*, 2 H); 3.46 (*s*, 2 H); 2.87 (*d*, *J* = 16, 2 H); 2.60 (*d*, *J* = 16, 2 H); 2.36 (br. *s*, OH); 2.18 (br. *s*, OH); 1.14 (*s*, 3 H). ^{13}C-NMR: 143.0 (*s*); 142.1 (*s*); 139.0 (*s*); 125.4 (*d*); 124.8 (*d*); 123.8 (*d*); 70.2 (*t*); 65.2 (*t*); 45.1 (*s*); 42.6 (*t*); 42.4 (*t*); 24.0 (*q*). MS: 192 (49, M^+), 174 (14), 159 (19), 143 (52), 129 (100), 115 (38), 105 (15), 91 (49), 77 (16), 65 (8), 63 (7), 51 (8), 39 (11), 31 (25).

(±)-2,5-Dimethylindane-2-methanol (= *(±)-2,3-Dihydro-2,5-dimethyl-1*H*-indene-2-methanol*; **29**). According to the *G.P.A*, with **28** (1.68 g, purity 98%, 8.7 mmol). Bulb-to-bulb distillation (oven temp. → 135/0.2 mbar) afforded **29** (1.40 g, 91%; purity 99%). Colorless oil. IR (neat): 3330 (br.), 2910, 1485, 1035, 810. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.04 (*d*, *J* = 8, 1 H); 6.98 (br. *s*, 1 H); 6.93 (br. *d*, *J* = 8, 1 H); 3.49 (*s*, 2 H); 2.87 (*d*, *J* = 16 1 H); 2.85 (*d*, *J* = 16, 1 H); 2.60 (*d*, *J* = 16, 2 H): 2.30 (*s*, 3 H); 1.80 (*s*, OH); 1.16 (*s*, 3 H). ^{13}C-NMR (90.5 MHz, $CDCl_3$): 142.6 (*s*); 139.4 (*s*); 135.8 (*s*); 127.0 (*d*); 125.5 (*d*); 124.5 (*d*); 70.5 (*t*); 45.0 (*s*); 42.7 (*t*); 42.4 (*t*); 24.0 (*q*); 21.2 (*q*). MS: 176 (33, M^+), 158 (11), 143 (100), 128 (35), 115 (21), 105 (21), 105 (11), 91 (11), 77 (8), 51 (6), 39 (7), 31 (15).

(±)-2,5-Dimethylindane-2-carboxaldehyde (= *(±)-2,3-Dihydro-2,5-dimethyl-1*H*-indene-2-carboxaldehyde*; **11**). According to the *G.P.B*, with **29** (0.65 g, purity 99%, 3.7 mmol). Bulb-to-bulb distillation (oven temp. 65°/0.2 mbar) afforded **11** (0.62 g, 92%; purity 95%). Colorless oil. IR: 3000, 2950, 2920, 2820, 2690, 1720, 1485, 1450, 1430, 810. ^{1}H-NMR: 9.63 (*s*, 1 H); 7.07 (*d*, *J* = 8, 1 H); 7.02 (br. *s*, 1 H); 6.97 (br. *d*, *J* = 8, 1 H); 3.31 (*d*, *J* = 16, 1 H); 3.29 (*d*, *J* = 16, 1 H); 2.71 (*d*, *J* = 16, 2 H); 2.31 (*s*, 3 H); 1.28 (*s*, 3 H). ^{13}C-NMR: 204.0 (*d*); 141.1 (*s*); 137.8 (*s*); 136.4 (*s*); 127.6 (*d*); 125.4 (*d*); 124.4 (*d*); 54.4 (*s*); 40.7 (*t*); 40.5 (*t*); 21.2 (*q*); 20.9 (*q*). MS: 174 (47, M^+), 159 (100), 145 (25), 130 (36), 128 (37), 115 (36), 105 (16), 91 (15), 77 (13), 65 (6), 63 (9), 51 (12), 39 (13), 29 (18).

(±)-(5-Ethyl-2-methylindan-2-yl)methyl Acetate (= *(±)-5-Ethyl-2,3-dihydro-2-methyl-1*H*-indene-2-methanol Acetate*; **30**). According to the *G.P.A*, with **27** (6.1 g, purity 96%, 23.8 mmol). Bulb-to-bulb distillation (oven temp. 130°/0.4 mbar) afforded **30** (5.70 g, 99%; purity 96%). Colorless liquid. IR: 3000, 2950, 2920, 2820, 1730, 1480, 1450, 1430, 1380, 1365, 1235, 1035, 820. ^{1}H-NMR: 7.07 (*d*, *J* = 8, 1 H); 7.00 (br. *s*, 1 H); 6.97 (br. *d*, *J* = 8, 1 H); 2.91 (*d*, *J* = 16, 1 H); 2.89 (*d*, *J* = 16, 1 H); 2.65 (*d*, *J* = 16, 1 H); 2.64 (*d*, *J* = 16, 1 H); 2.60 (*q*, *J* = 7, 2 H); 2.04 (*s*, 3 H); 1.21 (*t*, *J* = 7, 3 H); 1.17 (*s*, 3 H). ^{13}C-NMR: 171.3 (*s*); 142.5 (*s*); 142.2 (*s*); 139.3 (*s*); 126.0 (*d*); 124.6 (*d*); 124.3 (*d*); 71.3 (*t*); 43.3 (*t*); 43.0 (*s*); 42.7 (*t*); 28.7 (*t*); 24.3 (*q*); 20.9 (*q*); 15.9 (*q*). MS: 232 (7, M^+), 172 (50), 157 (100), 143 (79), 129 (65), 115 (23), 91 (14), 77 (7), 65 (3), 63 (3), 51 (4), 43 (63), 39 (5).

(±)-5-Ethyl-2-methylindane-2-methanol (= *(±)-5-Ethyl-2,3-dihydro-2-methyl-1*H*-indene-2-methanol*; **31**). To a stirred suspension of $LiAlH_4$ (1.35 g, 35.6 mmol) in Et_2O (30 ml) at r.t. was added dropwise a soln. of **30** (5.50 g, purity 96%, 23.7 mmol) in Et_2O (50 ml), and the mixture was stirred during 1 h. The mixture was cooled to 4°, 10% aq. NaOH soln. (6.8 ml) was added cautiously, and the mixture was stirred during 1 h (→ r.t.). Na_2SO_4 was added and the mixture filtered and evaporated to a colorless oil (4.8 g). Bulb-to-bulb distillation (oven temp. 100–140°/0.3 mbar) gave **31** (4.49 g, 99%; purity 99%). Colorless oil. IR: 3330 (br.), 3000, 2960, 2920, 2860, 2820, 1485, 1450, 1430, 1370, 1035, 820. ^{1}H-NMR: 7.07 (*d*, *J* = 8, 1 H); 7.00 (br. *s*, 1 H); 6.96 (br. *d*, *J* = 8, 1 H); 3.49 (*s*, 2 H); 2.87 (*d*, *J* = 16, 1 H); 2.85 (*d*, *J* = 16, 1 H); 2.62 (*d*, *J* = 16, 1 H); 2.61 (*d*, *J* = 16, 1 H); 2.60

(*q*, *J* = 7, 2 H); 1.83 (br. *s*, OH); 1.21 (*t*, *J* = 7, 3 H); 1.16 (*s*, 3 H). ^{13}C-NMR: 142.7 (*s*); 142.4 (*s*); 139.7 (*s*); 125.9 (*d*); 124.6 (*d*); 124.3 (*d*); 70.6 (*t*); 45.0 (*s*); 42.7 (*t*); 42.4 (*t*); 28.7 (*t*); 24.1 (*q*); 15.9 (*q*). MS: 190 (55, M^+), 172 (18), 157 (100), 143 (80), 129 (80), 115 (44), 91 (30), 77 (13), 65 (7), 63 (7), 51 (8), 39(10), 31 (21).

(±)-5-Ethyl-2-methylindane-2-carboxaldehyde (= *(±)-5-Ethyl-2,3-dihydro-2-methyl-1*H*-indene-2-carboxaldehyde*; **12**). According to the *G.P.B*, with **31** (3.49 g, 18.4 mmol). Bulb-to-bulb distillation (oven temp. 90–125°/0.4 mbar) afforded **12** (3.31 g, 91%; purity 95%). Colorless oil. IR: 3000, 2960, 2920, 2860, 2820, 2690, 1720, 1485, 1445, 1430, 880, 820. ^{1}H-NMR: 9.62 (*s*, 1 H); 7.09 (*d*, *J* = 8, 1 H); 7.03 (br. *s*, 1 H); 6.98 (br. *d*, *J* = 8, 1 H); 3.32 (*d*, *J* = 16, 1 H); 3.30 (*d*, *J* = 16, 1 H); 2.72 (*d*, *J* = 16, 1 H); 2.71 (*d*, *J* = 16, 1 H); 2.60 (*q*, *J* = 7, 2 H); 1.27 (*s*, 3 H); 1.21 (*t*, *J* = 7, 3 H). ^{13}C-NMR: 204.0 (*d*); 143.0 (*s*); 141.1 (*s*); 138.1 (*s*); 126.5 (*d*); 124.5 (*d*); 124.1 (*d*); 54.4 (*s*); 40.8 (*t*); 40.5 (*t*); 28.7 (*t*); 20.9 (*q*); 15.8 (*q*). MS: 188 (56, M^+), 173 (100), 159 (49), 145 (47), 129 (62), 115 (46), 91 (30), 77 (16), 63 (11), 51 (12), 39 (13), 29 (18).

(±)-2-(2-(Hydroxymethyl)-2-methylindan-5-yl)-propan-2-ol (= *(±)-2,3-Dihydro-α^5,α^5,2-trimethyl-1*H*-indene-2,5-dimethanol*; **32**). A stirred 22% MeMgCl soln. in THF (32 ml, 95 mmol; *Fluka*) at r.t. was diluted with THF (100 ml), and a soln. of **27** (5.87 g, purity 95%, 23.8 mmol) in THF (30 ml) was added dropwise during 10 min (exothermic: temp. → 51°). The mixture was heated to 60° during 1.5 h, cooled, and poured on Et_2O sat. aq. NH_4Cl soln. ice. The org. phase was washed with sat. aq. $NaHCO_3$ soln. and brine, dried (Na_2SO_4), and evaporated to a cloudy oil which solidified on standing. Crystallization from CH_2Cl_2 at 0° gave **32** (4.08 g, 76%; purity 98%). Colorless crystals. M.p. 122.5–123°. IR (solid): 3264, 2970, 2925, 2860, 1465, 1416, 1360, 1258, 1151, 1030, 956, 911, 841, 820. ^{1}H-NMR ((D_6)acetone): 7.32 (br. *s*, 1 H); 7.25 (br. *d*, *J* = 8, 1 H); 7.05 (*d*, *J* = 8, 1 H); 3.84 (*m*, 2 OH); 3.42 (*d*, *J* = 6, 2 H); 2.93 (*d*, *J* = 16, 1 H); 2.90 (*d*, *J* = 16, 1 H); 2.55 (*d*, *J* = 16, 1 H); 2.53 (*d*, *J* = 16, 1 H); 1.48 (*s*, 6 H); 1.13 (*s*, 3 H). ^{13}C-NMR: ((D_6)acetone): 149.4 (*s*); 142.3 (*s*); 141.3 (*s*); 124.7 (*d*); 123.3 (*d*); 121.8 (*d*); 72.0 (*s*); 69.9 (*t*); 46.0 (*s*); 43.4 (*t*); 42.9 (*t*); 32.6 (2*q*); 24.6 (*q*). MS: 220 (8, M^+), 205 (45), 202 (4), 145 (17), 128 (13), 115 (11), 91 (8), 59 (12), 43 (100), 31 (9).

(±)-5-Isopropyl-2-methylindane-2-methanol (= *(±)-2,3-Dihydro-5-isopropyl-2-methyl-1*H*-indene-2-methanol*; **33**). According to the *G.P.A*, with **32** (4.08 g, purity 98%, 23.8 mmol). Bulb-to-bulb distillation (oven temp. 125–160°/0.5 mbar) afforded **33** (3.56, 94%; purity > 99%). Colorless oil. IR: 3330 (br.), 2960, 2920, 2860, 1485, 1455, 1430, 1375, 1035, 820. ^{1}H-NMR: 7.07 (*d*, *J* = 8, 1 H); 7.02 (br. *s*, 1 H); 6.98 (br. *d*, *J* = 8, 1 H); 3.48 (*s*, 2 H); 2.88 (*d*, *J* = 16, 1 H); 2.85 (*d*, *J* = 16, 1 H); 2.85 (*sept.*, *J* = 7, 1 H); 2.62 (*d*, *J* = 16, 1 H); 2.60 (*d*, *J* = 16, 1 H); 2.00 (*s*, OH); 1.23 (*d*, *J* = 7, 6 H); 1.16 (*s*, 3 H). ^{13}C-NMR: 147.1 (*s*); 142.6 (*s*); 139.8 (*s*); 124.5 (*d*); 124.4 (*d*); 122.8 (*d*); 70.5 (*t*); 45.0 (*s*); 42.8 (*t*); 42.4 (*t*); 33.9 (*d*); 24.2 (2*q*); 24.1 (*q*). MS: 204 (49, M^+), 189 (33), 171 (100), 157 (21), 143 (62), 129 (70), 115 (36), 91 (30), 77 (13), 65 (7), 63 (6), 51 (6), 43 (25), 41 (15), 39 (10), 31 (19).

(±)-5-Isopropyl-2-methylindane-2-carboxaldehyde (= *(±)-2,3-Dihydro-5-isopropyl-2-methyl-1*H*-indene-2-carboxaldehyde*; **13**). According to *G.P.B*, with **36** (2.41 g, 11.8 mmol). Bulb-to-bulb distillation (oven temp. 85–145°/0.2 mbar) gave **13** (2.26 g, 93%; purity 98%). Colorless oil. IR: 2950, 2920, 2850, 2690, 1720, 1485, 1450, 1425, 880, 820. ^{1}H-NMR: 9.63 (*s*, 1 H); 7.10 (*d*, *J* = 8, 1 H); 7.07 (br. *s*, 1 H); 7.02 (br. *d*, *J* = 8, 1 H); 3.33 (*d*, *J* = 16, 1 H); 3.31 (*d*, *J* = 16, 1 H); 2.87 (*sept.*, *J* = 7, 1 H); 2.73 (*d*, *J* = 16, 1 H); 2.71 (*d*, *J* = 16, 1 H); 1.29 (*s*, 3 H); 1.22 (*d*, *J* = 7, 6 H). ^{13}C-NMR: 204.0 (*d*); 147.7 (*s*); 141.1 (*s*); 125.1 (*d*); 124.5 (*d*); 122.7 (*d*); 54.3 (*s*); 40.9 (*t*); 40.6 (*t*); 34.0 (*d*); 24.2 (2*q*); 21.0 (*q*). MS: 202 (66, M^+), 187 (99), 159 (61), 145 (100), 143 (64), 131 (60), 128 (61), 115 (51), 91 (36), 77 (19), 65 (10), 63 (10), 51 (11), 43 (36), 41 (19), 49 (15), 29 (15).

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